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Accurate density functional calculations on frequency-dependent hyperpolarizabilities of small molecules

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In this paper we present time-dependent density functional calculations on frequency-dependent first (β) and second (γ) hyperpolarizabilities for the set of small molecules, N_2, CO_2, CS_2, C_2H_4, NH_3, CO, HF, H_2O, and CH_4, and compare them to Hartree–Fock and correlated *ab initio* calculations, as well as to experimental results. Both the static hyperpolarizabilities and the frequency dispersion are studied. Three approximations to the exchange-correlation (xc) potential are used: the widely used Local Density Approximation (LDA), the Becke–Lee–Yang–Parr (BLYP) Generalized Gradient Approximation (GGA), as well as the asymptotically correct Van Leeuwen–Baerends (LB94) potential. For the functional derivatives of the xc potential the Adiabatic Local Density Approximation (ALDA) is used. We have attempted to estimate the intrinsic quality of these methods by using large basis sets, augmented with several diffuse functions, yielding good agreement with recent numerical static LDA results. Contrary to claims which have appeared in the literature on the basis of smaller studies involving basis sets of lesser quality, we find that the static LDA results for β and γ are severely overestimated, and do not improve upon the (underestimated) Hartree–Fock results. No improvement is provided by the BLYP potential which suffers from the same incorrect asymptotic behavior as the LDA potential. The results are however clearly improved upon by the LB94 potential, which leads to underestimated results, slightly improving the Hartree–Fock results. The LDA and BLYP potentials overestimate the frequency dependence as well, which is once again improved by the LB94 potential. Future improvements are expected to come from improved models for asymptotically correct exchange-correlation potentials. Apart from the LB94 potential used in this work, several other asymptotically correct potentials have recently been suggested in the literature and can also be expected to improve considerably upon the relatively poor LDA and GGA results, for both the static properties and their frequency dependence. © *1998 American Institute of Physics.* [S0021-9606(98)30547-4]

I. INTRODUCTION

Density Functional Theory (DFT) has by now become a reliable standard tool for calculating ground-state properties such as energies, geometries and vibrational frequencies. Calculations on systems perturbed by electric or magnetic fields are less common in DFT and their accuracy is less well established, especially if the external fields are frequency-dependent. This situation is rather different in Hartree–Fock based *ab initio* quantum chemistry. There, many techniques have been developed and implemented for analytically calculating properties such as frequency-dependent hyperpolarizabilities, the subject of this paper. Several studies have appeared using time-dependent Hartree–Fock (TDHF), as well as time-dependent MP2 or coupled cluster techniques.

Obviously, the more involved of these correlated approaches are very accurate, but at the same time computa-

tionally demanding. The Hartree–Fock results are not always of satisfactory accuracy for frequency-dependent hyperpolarizabilities, because of the importance of correlation for this property. The Hartree–Fock results are usually considerably too low with respect to the experimental or correlated *ab initio* theoretical numbers. For system sizes where the cost of the correlated *ab initio* techniques becomes prohibitive, one would like to have an approach which includes both correlation and frequency dispersion, as both are known to be important for a comparison with experimental hyperpolarizabilities. The time-dependent extension of density functional theory (TDDFT), provides an attractive framework for such an approach.

Until recently, TDDFT has been applied to atomic problems only, in which case the spherical symmetry greatly reduces the complexity of the equations. Recently however,

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molecular applications of TDDFT have started to appear in the literature, based on implementations in standard codes such as ADF, DEMON and TURBOMOLE. While in our case the initial focus was on frequency-dependent multipole polarizabilities and related properties,[1–6] such as Van der Waals dispersion coefficients and Raman scattering, other groups[7–14] primarily directed their attention to excitation energies, which can be found from the poles of the frequency-dependent polarizability, in a manner closely related to the TDHF approach.

These are all applications in the linear response regime with respect to the electric field, but we have recently been able to extend the scope of applications to the domain of the frequency-dependent hyperpolarizabilities,[5,15] also called nonlinear polarizabilities. These properties determine the nonlinear optical (NLO) response of a molecule when irradiated with one or more beams of light with possibly different frequencies. Second Harmonic Generation (SHG), or frequency doubling, is only one of the effects governed by hyperpolarizabilities.

Our initial application of our implementation for the frequency-dependent hyperpolarizabilities was to the C_{60} molecule,[5] for which we found agreement with one of the more recent experimental results,[16] which limits the second hyperpolarizability γ of C_{60} to a relatively low value. Although there is a large scatter in both the experimental and theoretical results, there seems to be a growing consensus on both the theoretical[5,17] and experimental[16,18] sides that the hyperpolarizability of C_{60} is much smaller than initially thought.

The paper on C_{60} contains the main points concerning the equations that we use, and a more detailed account of the theory underlying our implementation for the frequency-dependent hyperpolarizabilities is presented elsewhere.[15] That paper also contains examples on the numerical stability of our implementation on the He atom, and the CO and paranitroaniline molecules.

In short, the DFT expressions for the frequency-dependent hyperpolarizabilities, as well as the methods for calculating them, are very similar to those used in TDHF. In particular, our implementation makes uses of the $(2n+1)$-theorem which allows a direct calculation of the first hyperpolarizability tensor β, once a few linear response equations have been solved. We obtain β analytically in this manner and obtain γ from a finite field differentiation of β.[5,15]

In this paper, we shall apply our implementation to the calculation of frequency-dependent hyperpolarizabilities β and γ of a set of 9 small molecules. This is done for two reasons. The static DFT results for β and γ which have appeared in the literature until now, have lead to misleading optimistic conclusions about their quality, due to the use of relatively small basis sets. A recent numerical study[19] has clearly shown that the basis sets which were used, even in one of the most thorough of these studies,[20] were too small to come close to the basis set limits for β and γ, although very good and reliable results were obtained for the linear polarizability α. So, the first aim is to provide accurate static β and γ results, for many small molecules, in order to assess to

quality of both LDA and GGA potentials, as well as the Van Leeuwen–Baerends,[21] (LB94) potential. The latter belongs to the set of asymptotically correct (behaving as $-1/r$ for $r \to \infty$) potentials, which one might hope will remove the clear overestimations resulting from the use of asymptotically incorrect LDA or GGA exchange-correlation (xc) potentials.

In the second place, the frequency dependence of the hyperpolarizabilities is very important, as there may be large differences between the static results and the results at the frequency at which the experiment is actually performed. Here, we document how the different potentials behave in this respect. This point is especially important with respect to the TDHF frequency dispersion, as in many *ab initio* papers it has been assumed that the percentage frequency dispersion from the Hartree–Fock calculation can be used in combination with a correlated static value to obtain an estimate for the correlated dynamic value. Only a limited number of studies are available in which the important frequency dispersion is treated in a correlated manner. In short, the intention of this paper is to provide an accurate set of data on frequency-dependent hyperpolarizabilities of small molecules, upon which reliable conclusions can be based regarding the quality of various DFT approaches for this property. Another goal is to provide information on how the DFT results could be improved upon in future work.

II. DETAILS OF THE CALCULATION

A. Approximations for xc functionals

The solution of the TDDFT response equations proceeds in an iterative fashion, starting from the usual ground-state or zeroth-order Kohn–Sham (KS) equations. For these, one needs an approximation to the usual static xc potential $v_{xc}(\mathbf{r})$. After the ordinary KS equations have been solved, the first-order density change has to be calculated from an iterative solution to the first-order KS equations.[1,22] In these first order equations, an approximation is needed to the first functional derivative of the time-dependent xc potential $v_{xc}(\mathbf{r},t)$ with respect to the time-dependent density $\rho(\mathbf{r}',t')$.[23,5,15] For the analytic determination of the first hyperpolarizability β, one additionally needs the second functional derivative g_{xc}. These so-called xc kernels, given by the equations

$$f_{xc}(\mathbf{r},\mathbf{r}',t,t') = \frac{\delta v_{xc}(\mathbf{r},t)}{\delta \rho(\mathbf{r}',t')}, \tag{1}$$

$$g_{xc}(\mathbf{r},\mathbf{r}',\mathbf{r}'',t,t',t'') = \frac{\delta^2 v_{xc}(\mathbf{r},t)}{\delta \rho(\mathbf{r}',t') \delta \rho(\mathbf{r}'',t'')}, \tag{2}$$

determine the xc part of the screening of the externally applied electric field. Here, we use the so-called Adiabatic Local Density Approximation (ALDA) for the kernels. In this approximation (used almost without exception in the applications of TDDFT mentioned before), the time dependence (or frequency dependence if one talks about the Fourier-transformed kernel) is neglected, and one simply uses the differentiated static LDA expression. In our case, we use the Vosko–Wilk–Nusair[24] parametrization. An overview of the

TABLE I. Approximations for xc functionals used in this work.

v_{xc}	f_{xc}	g_{xc}
LDA	ALDA	ALDA
BLYP	ALDA	ALDA
LB94	ALDA	ALDA

TABLE II. STO basis set used for C, including diffuse functions.

| Standard basis functions | | Diffuse basis functions | |
nl value	Exponent	nl value	Exponent
1S	5.40	4S	0.57767
2S	1.28	4S	1.07281
2S	2.10	3P	0.50662
2S	4.60	3P	0.94086
2P	0.82	3D	0.54597
2P	1.48	3D	1.01395
2P	2.94	4F	1.0000
3D	2.2	4F	0.3000
4F	3.3		

approximations used in this work (including the approximations used for the xc potential) is given in Table I.

Our reasons for using the ALDA are two-fold. In the first place, it is computationally efficient, due to the LDA assumption of spatial locality. In the second place, there are no indications that other existing approximations improve upon the ALDA xc kernels. This may seem surprising because improved functionals exist both for the xc energy functionals and for the xc potential, but it should be kept in mind that an improvement to a functional does not automatically imply an improvement to its functional derivative. One example of this is provided by the high quality GGA xc energy functionals, which lead to relatively poor xc potentials, which do not improve on the LDA potential. Similarly, the LB94 xc potential is asymptotically much better than the LDA potential, but the use of its functional derivative does not improve the results of response calculations.

B. Technical details on the calculations

For many of our calculations, we have compared to a paper by Sekino and Bartlett.[25] For the sake of making a reliable comparison, we have used the geometries specified by them.[25] All geometries for CO_2, H_2O, HF, NH_3, CO, N_2, C_2H_4 are equilibrium geometries as in Ref. 25 (the $r(CO)$ distance for CO_2 reported in Ref. 25 contains a typographical error and should be corrected to 1.16226 Å). For CH_4, we used the same geometry as Maroulis[26] of $r(CH) = 2.052$ bohr, and for CS_2 the geometry of Ref. 27 was used.

Our basis sets are based upon the largest basis sets occurring in the Amsterdam Density Functional (ADF) basis set database.[28] This basis is a valence triple-zeta Slater-type orbital (STO) basis set with 2 polarization functions (3Z2P). We have added two diffuse s, two diffuse p, two diffuse d, and two diffuse f functions to these basis sets. The basis sets (and accompanying auxiliary basis sets for the fitting of the Coulomb potential) are available for the interested reader.[29]

Because of the fact that many diffuse functions are added per atom, linear combinations of these Atomic Orbitals (AOs) occur which are nearly linear dependent, which may lead to numerical problems. We use the occurrence of small eigenvalues of the overlap matrix as an indication that one has to be careful in the interpretation of the results. In some calculations we have removed the linear combinations of basis functions belonging to the smallest eigenvalues from the basis set. Typically, the functions belonging to eigenvalues smaller than 10^{-4} were removed. If this leads to a large change in the results although the number of rejected functions is small, the results in the full basis are considered unreliable. If the change in the results is small on the other hand, the complete basis set results are considered to be the

more reliable ones, as they were obtained with the larger basis set. In such cases, the complete basis set results were usually somewhat larger.

It should be clear that the goal of reaching the basis set limit and the goal of optimizing the stability of the results are somewhat contradictory. We have remedied this by performing calculations in different basis sets and with different criteria for rejecting basis functions. Comparison of the results lead to a selection of the most reliable combination of basis set and rejection criterion. For all results reported here, the basis set described above was used, and either no basis functions were rejected, or only a few resulting from the rejection criterion of 10^{-4}. As an example of a typical basis set used in these calculations, we present the basis functions for the carbon atom in Table II.

From the comparison of our results obtained with different large basis sets and different rejection criteria, as well as from the comparison of our results with numerical static LDA results,[19] we can estimate our results for the average β and γ values reported here to be within 10% or better from the basis set limit, which is more than sufficient for our present purposes. The changes resulting from improvements in numerical integration accuracy or in the convergence of the ordinary KS equations are estimated to be negligible ($<1\%$).

In the following tables, we report all independent components of the static hyperpolarizability tensors β and γ, and compare them to correlated *ab initio* results. We additionally report the average hyperpolarizabilities $\beta_\parallel$ and $\gamma_\parallel$, defined by:

$$\beta_\parallel = \frac{1}{5} \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji}),$$

$$\gamma_\parallel = \frac{1}{15} \sum_{i,j} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}),$$

(3)

where i refers to the dipolar axis in the formula for $\beta_\parallel$.

The average hyperpolarizabilities are reported for both the static and the frequency-dependent properties, such as second harmonic generation (SHG), optical rectification (OR), electro-optic Pockels effect, electric field induced second harmonic generation (EFISH), and the electro-optic Kerr effect (EOKE). For the frequency-dependent results, we compare to experimental values as well as to theoretical results. For the EOPE and EOKE effects the comparison to the

TABLE III. Results for hyperpolarizability of N_2.

	TDHF[a]	MBPT(2)[a]	CCSD[a]	CCSD(T)[a]	EXP	LDA	BLYP	LB94
γ_{xxxx}	660	780	810;[a] 782[b]	860		1100	1200	610
γ_{zzzz}	790	1220	1220;[a] 1180[b]	1290		1800	2000	1000
γ_{xxzz}	270	340	350;[a] 313[b]	370		450	510	260
$\gamma_{\parallel}$	730	930	950;[a] 903[b]	1010		1300	1400	740
THG	937	1200	1200;[a] 1212[b]	1300	1295 ± 206[c]	⋯	⋯	⋯
EFISH	822	1100	1100;[a] 1041[b]	1100	1057.6 ± 6.4;[d] 1030 ± 12[e]	1500	1800	840
IDRI	788	1000	1000;[a] 992[b]	1100		⋯	⋯	⋯
EOKE	756	1000	1000;[a] 947[b]	1100	1430 ± 160[f]	1400	1500	770

[a]Sekino and Bartlett, Ref. 25.
[b]Hättig *et al.*, Ref. 40.
[c]Ward and New, Ref. 58.
[d]References 59,60.
[e]Ward and Miller, Ref. 45.
[f]Buckingham *et al.*, Ref. 61 at $\lambda = 632.8$ nm ($\omega = 0.072$ a.u.).

experimental values is allowed under the assumption of Kleinman symmetry (which is rigorously true at zero frequency), because in that case, $\beta_{\parallel}^{EOPE}$ and $\gamma_{\parallel}^{EOKE}$ are equal to the experimentally measured quantities β^K and γ^K, as defined in, for example, Ref. 30. This has been done in order to compare our values directly to those reported by Sekino and Bartlett.[25] Our attention will however be directed almost exclusively to the SHG and EFISH tensors, for which a direct comparison to experiment is allowed.

III. RESULTS AND DISCUSSION

A. General remarks

For most molecules we compare to the results obtained by Sekino and Bartlett,[25] who have obtained Hartree–Fock (HF), second-order many-body perturbation theory [MBPT(2)], coupled cluster singles and doubles (CCSD) and coupled cluster singles and doubles with an approximated triples contribution [CCSD(T)] results. The amount of correlation in these calculations and the quality of the hyperpolarizability results ranges from the relatively poor HF results to the highly accurate, highly correlated CCSD(T) results. As no frequency-dependent coupled cluster approaches were available at the time, Sekino and Bartlett estimated the correlated frequency-dependent results from the percentage frequency dispersion obtained in the HF calculation. For reviews on (frequency-dependent) hyperpolarizabilities, we refer to Shelton and Rice[31] and Bishop.[30]

Unless explicitly stated otherwise, all frequency-dependent results refer to a fundamental frequency of $\omega = 0.0656$ a.u., which is equivalent to a wavelength of $\lambda = 694.3$ nm. For the static results, we also compare to previous DFT results, which have been obtained by Dickson and Becke,[19] by Guan *et al.*,[20] and by Dixon and Matsuzawa.[32] The results by Dickson and Becke are particularly important, as they have obtained finite field LDA (although in a slightly different parametrization) values for several molecules treated here, with a basis set free method. Although there are still uncertainties in their results of an estimated 10%, due to numerical difficulties in the finite field procedure, their values can be used for judging if results obtained in a finite basis set have converged with respect to

basis set size. In this respect, the Dixon and Matsuzawa results seem insufficiently accurate for statements about the intrinsic quality of the DFT results. The results by Guan *et al.* are clearly more accurate than those, but they also seem to have included an insufficient number of diffuse functions for basis set limit results. From the numbers below, it can be seen that our values are typically much closer to the basis set free results, and reliable conclusions on the intrinsic quality of DFT calculations on frequency-dependent hyperpolarizabilities can therefore be drawn from them.

In this work, we concentrate on the electronic hyperpolarizabilities. This is usually the largest part of the frequency-dependent hyperpolarizabilities, although zero point vibrational averaging can be significant (typically 10% of the electronic value), and also the purely vibrational contribution[33–36] can be large in some cases, especially for the static values.

In addition to the results presented here, we have performed some test calculations on the H_2, CH_3F, CH_2O, CH_3CN, and H_2S molecules, for some of which Colwell *et al.*[37,38] have previously obtained static DFT results for β. The results by Colwell *et al.* and those from our test calculations are in agreement with the conclusions which will be drawn from the values obtained here.

B. N_2

For N_2 in Table III, our static LDA value for γ_{xxxx} is in agreement with the finite field, basis set free LDA result obtained by Dickson and Becke.[19] We obtain $\gamma_{xxxx} = 1100$ a.u., compared to their result of 1100 ± 200, where the error bar in their result gives the uncertainty from the polynomial fit to the results at different field strengths. For the other components no stable results were obtained by Dickson and Becke. Although the relative magnitude of the tensor components is reasonably well described by the LDA and BLYP potentials, all the components are too large. This leads to a clear overestimation in $\gamma_{\parallel}$, in comparison to the accurate CCSD(T) value. The LB94 result of 740 a.u. is too low on the other hand, and close to the HF value of 730 a.u. (Luo *et al.*[39] obtained a HF value of 716 a.u.). One other typical feature is the overestimation of the frequency dependence by

TABLE IV. Results for the hyperpolarizability of CO_2.

	TDHF[a]	MBPT(2)[a]	CCSD[a]	CCSD(T)[a]	EXP	LDA	BLYP	LB94
γ_{xxxx}	700	1010	930	900		1300	1600	740
γ_{zzzz}	810	1120	900	1030		1900	2300	1100
γ_{xxzz}	330	500	490	520		710	870	380
$\gamma_\parallel$	800	1170	1070	1150		1700	2000	910
THG	1046	1500	1400	1500	1860 ± 270[b]	⋯	⋯	⋯
EFISH	910	1300	1200	1300	1332 ± 15[c]	2000	2500	1000
IDRI	871	1300	1200	1200		⋯	⋯	⋯
EOKE	833	1200	1100	1200		1800	2200	960

[a]Reference 25.
[b]Reference 62.
[c]Reference 45.

the LDA and BLYP potentials. In this respect, the LB94 potential behaves again similarly to the HF result. Presumably, the recent CCSD results by Hättig et al.,[40] in which the frequency dependence was also treated at the CC level, instead of the HF estimate used by Sekino and Bartlett,[25] can be regarded as the benchmark theoretical results at the moment, which are in excellent agreement with experiment (except for the experimental EOKE result, which might be unreliable[40]). Comparing to their results, we find that the 14.4% LB94 frequency dispersion (calculated from the ratio between the EFISH and static γ results) compares quite well to their value of 15.3%.

Finally, we mention the MP4 result by Maroulis and Thakkar[41] of $\gamma_\parallel = 830$ a.u., and the multiconfiguration SCF (MCSCF) value of 885 a.u. by Luo et al.,[39] which are superior to our DFT results. Dixon and Matsuzawa obtained LDA values of $\gamma_\parallel = 1120$ and 1280 a.u., depending on the field strengths used in their FF calculations, in agreement with LDA results obtained in this work and those by Dickson and Becke.

C. CO_2 and CS_2

The CO_2 results in Table IV show the same trends as the N_2 results. There is a clear overestimation in the LDA and BLYP values, both for the static γ-tensor and for the percentage frequency dispersion. The LB94 results are once more too low, but they are better than the HF values, which are even lower. For CO_2, as well as for CH_4, NH_3, H_2O, and HF, the pure vibrational frequency-dependent hyperpolarizabilities have been determined by Bishop and Dalskov.[35]

For the EFISH effect, the vibrational contribution is relatively small for these molecules. It is much larger for the static values. Apart from the pure vibrational hyperpolarizabilities from the paper just mentioned, the effect of zero point vibrational averaging can be significant. However, the data are scarce on this, for which reason we will restrict ourselves in this work to the discussion of the pure vibrational hyperpolarizabilities.

Similar trends as for CO_2, are observed for CS_2 in Table V (where different frequencies have been used than in the previous table). The experimental EFISH value was obtained for liquid CS_2 and is therefore not directly comparable to the theoretical results. The experimental EOKE value also seems to be very high in comparison to all theoretical values in the table. It was recently shown by Champagne,[42] who determined the nuclear relaxation contribution to the frequency-dependent hyperpolarizabilities, that the discrepancy between the experimental and theoretical results cannot be explained from the vibrational contribution to the hyperpolarizability. He therefore recommends a reinvestigation of the experimental results. The need for such a reinvestigation is supported by our present results as well as by the caution which is expressed in the experimental EOKE paper[43] on the reliability of the obtained EOKE γ-value. For this reason, we take the CCSD(T) values as the reference, and note the usual overestimation for the LDA and BLYP results and an underestimation for the LB94 results, which are slightly lower than the HF values here. For the CS_2 molecule, our results may be influenced by the HF geometry which we have used

TABLE V. Results for the hyperpolarizability of CS_2.

	TDHF[a]	MP2[a]	CCSD[a]	CCSD(T)[a]	EXP	LDA	BLYP	LB94
γ_{xxxx}	7379	8970	8650	9030	⋯	11600	14700	6700
γ_{zzzz}	10962	11330	10730	14000	⋯	25800	30900	13400
γ_{xxzz}	6557	9030	8550	8860	⋯	9400	11700	5300
$\gamma_\parallel$	11373	14270	13600	14700	⋯	18800	23400	10400
EFISH	13680	17163	16358	17681	(38000)[b]	23100[b]	29900[b]	12200[b]
EOKE	13297	16684	15900	17187	(114000)[c]	22800[c]	29400[c]	12100[c]

[a]All ab initio results obtained by Ohta et al., Ref. 27.
[b]Experimental result at $\lambda = 1064$ nm ($\omega = 0.0428$ a.u.) in a solvent by Levine and Bethea (Ref. 63) with a 15% error margin. All theoretical results are obtained at the same wavelength.
[c]Experiment at $\lambda = 633$ nm ($\omega = 0.072$ a.u.) by Bogaard et al., Ref. 43, who express caution about the reliability of their γ value. Theoretical results at the same wavelength.

TABLE VI. Results for the hyperpolarizability of C_2H_4.

	TDHF[a]	MBPT(2)[a]	CCSD[a]	CCSD(T)[a]	EXP	LDA	BLYP	LB94
γ_{xxxx}	3300	6100	5400	5600		7200	8100	4400
γ_{yyyy}	2800	3500	3200	3400		5400	6300	3300
γ_{zzzz}	11900	11800	9800	10200		12900	16800	5000
γ_{xxzz}	3100	3500	2900	3000		3900	4700	1800
γ_{yyzz}	2500	2600	2200	2300		3100	4000	1400
γ_{xxyy}	1600	2000	1800	1900		3000	3400	1900
$\gamma_{\parallel}$	6500	7500	6400	6700		9100	11100	4600
THG	17500	20300	17300	18200		…	…	…
EFISH	9900	11400	9700	10200	9030 ± 200[b]	14500	19400	6100
IDRI	8500	9800	8400	8800		…	…	…
EOKE	7400	8600	7300	7700		10500	13000	5000

[a]*Ab initio* results by Sekino and Bartlett, Ref. 25.
[b]Reference 62.

in order to allow for a direct comparison with the theoretical values obtained by Ohta *et al.*[27]

D. C_2H_4

The C_2H_4 results in Table VI are as expected from the previous tables. Overestimations for the LDA and BLYP potentials, and underestimations for the LB94 potential. Incidentally, the HF values are much better than the DFT ones here. The trends for the relative magnitudes of the various tensor components are well reproduced by the DFT schemes on the other hand. The importance of frequency dependence is large for this molecule, and a purely static approach would clearly be undesirable here. The C_2H_4 molecule is the first in a series of $C_{2n}H_{2n+2}$ polyene molecules, for which the density functional results have been studied in Ref. 44. For the larger molecules, all three xc potentials considered here show large overestimations for α and γ. The reason for this

behavior is one of the topics of our current research, but it is known to be unrelated to the LDA and GGA overestimations reported here.

E. NH_3

Our LDA results for NH_3 (Table VII) are in very good agreement with the basis set free LDA results by Dickson and Becke,[19] who obtained in a.u. (our own LDA values in parentheses) $\beta_{\parallel} = -55.(6)(-55.4), \beta_{zzz} = -64.(4) \ (-66.4), \beta_{zxx} = -14.(3) \ (-12.9),$ and $\beta_{xyy} = 8 \ (8.11),$ which further supports the quality of the basis sets we used. This should be contrasted to the LDA result obtained for the average β by Guan *et al.* of -37.2 a.u. and the one by Dixon and Matsuzawa[32] who basically obtained no converged result for β (deviations from -40 a.u. to -67 a.u.). Evidently, these

TABLE VII. Results for the hyperpolarizability of NH_3.

	TDHF	MBPT(2)	CCSD[a]	CCSD(T)[a]	EOM-CC[b]	EXP	LDA[c,d]	BLYP	LB94
β_{zzz}	-11.1;[a] -6.98[e]	-37.8;[a] -31.15[e]	-33.3	-39.6	-41.0		-66.4	-74.7	-30.7
β_{zxx}	-7.0;[a] -6.73[e]	-8.1;[a] -7.55[e]	-8.0	-8.8	-8.8		-12.9	-16.5	-10.0
β_{xyy}	9.41[e]	9.09[e]			7.2		8.11	9.38	8.20
$\beta_{\parallel}$	-15.1;[a] -12.26[e]	-32.5;[a] -27.75[e]	-30.0	-34.3	-35.0		-55.4	-64.6	-30.5
SHG	-21.98	-46.6	-42.5	-49.1	-41.5	-48.4 ± 1.2[f]	-109	-138	-46.0
OR/EOPE	-16.74;[a] -14.04[e]	-36.3;[e] -32.16[e]	-33.1	-38.3	…		-67.3	-80.1	-34.6
γ_{xxxx}	1200;[a] 1089[e]	1800;[a] 1487[e]	1700	1800			3300	3800	1600
γ_{zzzz}	4500;[a] 4300[e]	8000;[a] 7279[e]	7400	8200			15900	18700	4700
γ_{xxzz}	1100;[a] 1082[e]	1900;[a] 1487[e]	1800	2000			3800	4900	1300
$\gamma_{\parallel}$	2400;[a] 2307[e]	4100;[a] 4162[e]	3800	4200			8000	9400	2800
THG	4924	8300	7800	8500			…	…	…
EFISH	3276	5500	5200	5600		6147 ± 110[g]	15700	20300	4000
IDRI	2937	5000	4600	5100			…	…	…
EOKE	2652;[a] 2533[e]	4500;[a] 4162[e]	4200	4600			9700	11700	3100

[a]Reference 25.
[b]Reference 64.
[c]Guan *et al.* (Ref. 20) obtained two sets of LDA results for β with two different programs and basis sets: $\beta_{zzz} = -32.9$ and -28.2; $\beta_{zxx} = -10.36$ and -16.89; $\beta_{xyy} = 6.83$ and 11.98.
[d]Dixon and Matsuzawa calculated β at the LDA level using finite field results, but their static $\beta_{\parallel}$ values with different field strengths differed from -40 a.u. to -67 a.u. Their LDA values for the average γ ranged from 6300 a.u. to 7100 a.u.
[e]TDHF and QED-MP2 results by Aiga and Itoh, Ref. 46.
[f]Experimental value by Ward and Miller, Ref. 45.
[g]References 31 and 45.

TABLE VIII. Reslts for the hyperpolarizabilities of CO.

	TDHF [a]	MBPT(2)[a]	CCSD[a]	CCSD(T)[a]	EXP	LDA[b]	BLYP	LB94
β_{zzz}	28.2; 31.47[c]	25.6	26.1; 28.9[c]	26.0[d]		33.9[b]	34.4	24.8
β_{zxx}	3.5; 4.89[c]	6.0	6.1; 7.3[c]	6.6; 7.8[c]		8.43[b]	8.74	4.80
$\beta_{\parallel}$	21.1[e]	22.6	23.0; 26.1[c]	23.5; 26.6[c]		30.5	31.1	20.6
SHG	24.1	25.9	26.4	27.0; 30.1 ± 0.6[c]	29.9 ± 3.2[f]	36.6	37.8	23.4
OR/EOPE	21.9	23.6	24.1	24.6		32.3	33.1	21.5
γ_{xxxx}	920; 1173[c]	1380	1360; 1239[c]	1470; 1357[c]		2000[b]	2200	1000
γ_{zzzz}	1200; 1173[c]	1740	1740; 1616[c]	1880; 1758[c]		2700[b]	3000	1400
γ_{xxzz}	360; 348[c]	520	510; 460[c]	540; 500[c]		750	830	390
$\gamma_{\parallel}$	1020; 992[c]	1500	1480; 1353[c]	1590; 1475[c]		2200	2400	1100
THG	1484	2200	2200	2300		...	...	...
EFISH	1211	1800	1800	1900; 1790 ± 90[c]	1720 ± 48[g]	2900	3200	1400
IDRI	1138	1700	1700	1800		...	...	...
EOKE	1071	1600	1600	1700		2400	2700	1200

[a]*Ab initio* values in the tables taken from Sekino and Bartlett (Ref. 25), unless otherwise stated.
[b]Numerical LDA results by Dickson and Becke (Ref. 19) are $\beta_{zxx}=8.6$, $\beta_{zzz}=33.7$, $\gamma_{xxxx}=2100$, and $\gamma_{zzzz}=2700$, while Guan *et al.* (Ref. 20) obtained two sets of values for β: $\beta_{zzz}=$ 31.3 and 34.9; $\beta_{zxx}=$ 6.6 and 8.8.
[c]Values obtained by Maroulis, Ref. 47.
[d]Other CCSD(T) values: 28.6 (Ref. 47); 30.17 (Ref. 65).
[e]Other HF values: 24.75 (Ref. 47); 25.444 (Ref. 48).
[f]Reference 45. Experimental value referenced by Shelton and Rice (Ref. 31) is 30.2 ± 3.2.
[g]Reference 45. Experimental value referenced by Shelton and Rice (Ref. 31) is 1730 ± 50.

previous DFT studies were insufficiently accurate for making conclusions about the intrinsic (basis set limit) quality of DFT hyperpolarizabilities.

The NH$_3$ molecule has been studied intensively recently by Sekino and Bartlett, who performed equation-of-motion coupled cluster (EOM-CC) calculations in order to check the reliability of the TDHF frequency dispersion, which had previously been used by Sekino and Bartlett[25] to estimate the frequency-dependent CCSD(T) values for the numbers in our tables. Their static EOM-CC and CCSD(T) values for $\beta_{\parallel}$ of, respectively, -35.0 and -34.3 a.u. can be taken as the benchmark theoretical values. The LB94 result of -30.5 a.u., although slightly underestimated, compares favorably to these numbers in comparison to the HF, LDA, and BLYP values of -15.1, -55.4, and -64.6 a.u. A similar (small) underestimation for the LB94 result is found with respect to the β^{SHG} experimental number of -48.4 a.u.[45] For $\gamma_{\parallel}$, the LB94 value of 2800 a.u., although clearly underestimated, is in better agreement with the CCSD(T) result of 4200 a.u. than the HF, LDA, and BLYP values of, respectively, 2400, 8000, and 9400 a.u. The EOM-CC frequency dispersion for the EOPE first hyperpolarizability tensor of 18.6% is higher than the TDHF result of 10.9%. The QED-MP2 (Ref. 46) dispersion and the LB94 dispersion of 15.9% and 13.4% are also higher than the HF dispersion. The LDA and BLYP frequency dispersions are clearly overestimated (21.6% and 24.0%). The first and second vibrational frequency-dependent hyperpolarizabilities have been estimated to be relatively small for this molecule.[34,35]

F. CO

Our LDA results for CO in Table VIII are once more in excellent agreement with the numerical finite field results obtained by Dickson and Becke.[19] Their results (in a.u.) are $\beta_{zxx}=8.6$, $\beta_{zzz}=33.7$, $\gamma_{xxxx}=2100$, and $\gamma_{zzzz}=2700$,

whereas we obtained, respectively, $\beta_{zxx}=8.43$, $\beta_{zzz}=33.9$, $\gamma_{xxxx}=2000$, and $\gamma_{zzzz}=2700$, while similar results for β where obtained by Guan *et al.*[20] and by Dixon and Matsuzawa.[32] Again, the LDA and BLYP values are clearly too large, both for β and γ. The LB94 values are too low, on the other hand, but for γ they seem to be slightly preferable to the HF, LDA, and BLYP values. Using the large basis set CCSD(T) results by Maroulis[47] as the benchmark, the HF value for $\beta_{\parallel}$ [Maroulis obtained 24.75,[47] while other reported values are 21.1 (Ref. 25) and 25.44 (Ref. 48)] is better than the LDA, BLYP, and LB94 values of, respectively, 30.5, 31.1, and 20.6 a.u. For β^{SHG}, Maroulis' CCSD(T) value with TDHF frequency dispersion of 30.1 ± 0.6 is in excellent agreement with the experimental value of 29.9 ± 3.2.[45] The HF, LDA, BLYP, and LB94 values for β^{SHG} show the same trends as for the static $\beta_{\parallel}$ and as for the other molecules. For the static $\gamma_{\parallel}$ and for γ^{EFISH}, the LB94 values are somewhat better than the other computationally cheap approaches (HF, LDA, BLYP), although again underestimated with respect to the CC and experimental results.

G. HF

A comparison to the numerical LDA values of Dickson and Becke[19] for HF yields (our own values of Table IX in parentheses): $\beta_{zxx}=-2.3$ (-2.22); $\beta_{zzz}=-10.8$ (-10.9); $\gamma_{xxxx}=1100$ (1200); γ_{zzzz} 610 (630), which is quite satisfactory. Once again, the numerical and basis set errors in our results seem to be substantially smaller than the errors introduced through the approximations for the xc potential. Consequently, we are truly testing these xc potentials themselves and not the technical accuracy of the calculations.

For a long time, the benchmark coupled cluster *ab initio* values for β^{SHG} were not in satisfactory agreement with the experimental value of 10.9 ± 0.95.[49] For example, the original CCSD(T) value of Sekino and Bartlett[25] of -8.0 a.u. is

TABLE IX. Results for the hyperpolarizabilities of HF.

	TDHF	MBPT(2)	CCSD	CCSD(T)	EXP	LDA	BLYP	LB94
β_{zzz}	-8.40	-9.10	-9.24[a]	-9.62		-10.9	-11.7	-9.11
β_{zxx}	-0.28	-1.25	-1.03[a]	-1.27		-2.22	-2.10	-1.22
$\beta_{\parallel}$	-5.38[b,c]	-6.96	-6.78[a]	-7.30		-9.23	-9.54	-6.93
SHG	-5.853	-7.6	-7.4[a,d]	-8.0	-10.9 ± 0.95[e]	-10.7	-11.2	-7.68
OR/EOPE	-5.522	-7.2	-7.0[a]	-7.5		-9.68	-10.0	-7.17
γ_{xxxx}	350	640	600[a]	650		1200	1400	450
γ_{zzzz}	270	380	360[a]	390		630	690	340
γ_{xxzz}	100	170	160[a]	180		300	340	130
$\gamma_{\parallel}$	320	560	520[a]	560		1000	1100	410
THG	404	700	660[a]	710		...	...	...
EFISH	359	620	580[a,f]	630	830 ± 120[g]	1300	1400	470
IDRI	345	600	560[a]	610		...	...	...
EOKE	333	580	540[a]	590		1100	1200	430

[a]Frequency dispersion estimated from the TDHF results (Ref. 25).
[b]Bishop and Maroulis (Ref. 66) obtained HF values of $\beta_{\parallel}=-5.9$ a.u. and $\gamma_{\parallel}=334$ a.u.
[c]Papadopoulos et al. (Ref. 52) obtained HF values of $\beta_{\parallel}=-5.70$ a.u. and $\gamma_{\parallel}=303$ a.u., and MP4(SDTQ) values of $\beta_{\parallel}=-8.33$ and $\gamma_{\parallel}=579$ a.u.
[d]More recent EOM-CCSD results (Ref. 51) give -9.8 ± 0.5 (with orbital relaxation) or -10.2 ± 0.5 (without orbital relaxation); CCSD result by Hättig et al. (Ref. 50): 8.79.
[e]Reference 49.
[f]More recent EOM-CCSD results (Ref. 51) give 720 ± 40 (with orbital relaxation) of 730 ± 40 (without orbital relaxation).
[g]Reference 66.

too low. More recent results of -8.79 a.u. (Ref. 50) and estimated EOM-CC results[51] of -9.8 ± 0.5 and -10.2 ± 0.5 (with or without orbital relaxation) improve upon this. The LDA and BLYP values of -10.7 and -11.2 a.u. are in good agreement with the experimental values, which should however be considered fortuitous, in view of the systematic overestimations for the other molecules. In fact, these DFT results might suggest that the experimental number may be at the lower end of the given error bars. The LB94 value for β^{SHG} of -7.68 a.u. is satisfactorily close to the CCSD(T) value[25] and is better than the TDHF result of -5.9 a.u.

For γ^{EFISH}, the CCSD(T) value of 630 a.u. is too low with respect to the experimental value of 830 ± 120 a.u. The more recent EOM-CC values[51] of 720 ± 40 and 730 ± 40 (with or without orbital relaxation) improve upon this. For $\gamma_{\parallel}$, the HF and LB94 values of 320 and 410 a.u. are again too low, in comparison to the CCSD(T) value of 560 a.u., and the LDA and BLYP values too large (1000 and 1100 a.u.). The LB94 values are the preferable ones, which is also true for the frequency-dependent values.

The HF molecule was studied in detail by Papadopoulos et al.[52] in different basis sets, at the SCF, MP2, and MP4(SDTQ) levels of theory. These authors also provide extensive references to earlier calculations on this molecule. Bishop and Dalskov[35] conclude that the vibrational second hyperpolarizabilities are small for HF, in comparison to the electronic value.

H. H_2O

For the LDA values, we find again good agreement with Dickson and Becke's[19] results. Our static β values of Table X are slightly higher than theirs: $\beta_{zzz}=-21.2$ vs -20.1; $\beta_{zxx}=-12.1$ vs -11.9; $\beta_{zyy}=-9.47$ vs -9.2, and $\beta_{\parallel}=$

-25.7 vs -24.8, all in a.u. The agreement in the components of γ is even more satisfactory: $\gamma_{xxxx}=5200$ vs 5100; $\gamma_{yyyy}=1500$ vs 1400 and $\gamma_{zzzz}=2600$ vs 2600. In contrast, the LDA results for β_{zzz} obtained by Guan et al.[20] are too low (-17.1 and -13.2), and the results by Dixon and Matsuzawa[32] are insufficiently converged.

Our LDA and BLYP values for $\beta_{\parallel}$ are again clearly higher than the benchmark results, such as the recent CCSD(T) value of -17.5 ± 0.3 by Maroulis,[53] the recent experimental value (at $\lambda=1064$ nm) of -19.2 ± 0.9,[54] the somewhat older CCSD(T) value of -18.0 by Sekino and Bartlett,[25] and the MP4 and SDQ-MBPT(4) values of -19.4 and -16.8 by Maroulis[55] (MCSCF values[56] of -15.15 and -15.86 for two different active spaces are also available). A similar overestimation is found for $\gamma_{\parallel}$, for which the recent CCSD(T) (Ref. 53) and experimental[54] estimates of, respectively, 1710 ± 60 and 1800 ± 150 (at $\lambda=1064$ nm) can again be considered as the benchmark values. The LB94 values are quite satisfactory on the other hand. They are much better than the LDA, BLYP, as well as HF values, and in reasonable agreement with the CCSD(T) results. The LB94 frequency dispersion for SHG at $\omega=0.0656$ of 21.3% is in between the HF dispersion of 16.4% and the MCSCF value of 24.7%, in agreement with an estimate from the quasi-energy derivative MP2 values by Aiga and Itoh.[46] The LB94 potential gives a β^{SHG} value of -20.3, which is satisfactorily close to the experimental value[45] of -21.8 ± 0.9, especially if a 10% estimate for vibrational averaging[56] is added to the theoretical value. For γ, the LB94 results are poorer. Although still better than LDA, BLYP, or HF, the static γ and γ^{SHG} values are clearly too low.

TABLE X. Results for the hyperpolarizabilities of H_2O.

	TDHF [a]	MBPT(2) [a]	CCSD [a]	CSD(T) [a]	EXP	LDA	BLYP	LB94	MP4	SDQ-MBPT(4)
β_{zzz}	−7.1;[a] −7.8[b]	−13.7	−12.0	−13.7		−21.2	−22.0	−13.3		
β_{zxx}	−1.4;[a] −1.4[b]	−5.9	−5.2	−6.2		−12.1	−13.4	−10.0		
β_{zyy}	−8.3;[a] −9.4[b]	−9.4	−9.9	−10.2		−9.47	−9.80	−4.44		−10.0
$\beta_{\parallel}$	−10.8;[a] −11.2;[b,c] −8.40[b]	−17.5;[a] −13.11[b]	−16.2	−18.0[d]		−25.7	−27.1	−16.7	−19.4	−16.8
SHG	−12.568[a,c]	−20.4	−19.0	−21.1	21.8±0.9[e]	−34.4	−37.3	−20.3		
OR/EOPE	−11.290;[a] −8.75[b]	−18.4;[a] −13.73[b]	−17.1	−19.0		−28.1	−29.9	−17.8		
γ_{xxxx}	1500;[a] 1450[b]	2800	2700	2900		5200	6100	1700	2900[b]	2541[b]
γ_{yyyy}	550;[a] 572[b]	820	760	820		1500	1700	750	821[b]	807[b]
γ_{zzzz}	920;[a] 905[b]	1540	1390	1500		2500	2800	1100	1575[b]	1425[b]
γ_{xxzz}	400;[a] 389[b]	750	700	770		1300	1500	470	779[b]	669[b]
γ_{yyzz}	280;[a] 287[b]	430	410	440		780	880	360	464[b]	418[b]
γ_{xxyy}	350;[a] 342[b]	660	620	680		1300	1500	440	684[b]	596[b]
$\gamma_{\parallel}$	1010;[a] 992;[b] 853[b]	1780;[a] 1420[b]	1650	1800[d]		3200	3700	1200	1830	1628
THG	1515[a]	2700	2500	2700		...	...	...		
EFISH	1216[a]	2100	2000	2200	2310±120[e]	4800	5800	1500		
IDRI	1139[a]	2000	1900	2000		...	...	...		
EOKE	1069;[a] 906[b]	1900;[a] 1529[b]	1700	1900		3600	4200	1300		

[a]*Ab initio* values obtained by Sekino and Bartlett, Ref. 25.
[b]Static *ab initio* values by Maroulis, Ref. 55.
[c]Luo *et al.*, (Ref. 56) obtained CASSCF values for the static $\beta_{\parallel}$ of −15.25 and −15.86 for two different active spaces, and β^{SHG}=−19.02 for the first active space.
[d]Very recent benchmark values of $\beta_{\parallel}$=−17.5±0.3 and $\gamma_{\parallel}$=1710±60 have been obtained by Maroulis (Ref. 53) from large basis set CCSD(T) calculations. New experimental results have been obtained by Kaatz *et al.* (Ref. 54), who obtained (at λ=1064 nm) $\beta_{\parallel}$=−19.2±0.9 and $\gamma_{\parallel}$=1800±150.
[e]Experimental value by Ward and Miller, (Ref. 45).

I. CH$_4$

A comparison to Dickson and Becke's results for CH$_4$ yields: β_{xyz}=−7.5 a.u. ± 10% (Ref. 19) vs −8.63 a.u. (this work, Table XI) and γ_{zzzz}=3700 a.u. ± 10% (Ref. 19) vs 3700 a.u. (this work). Our value for β_{xyz} is somewhat outside the error bars given by Dickson and Becke, which is a reason for caution in the interpretation of the results. The good agreement in the γ-value on the other hand supports the reliability of our basis sets. Surprisingly, the LB94 value for β_{xyz} is too high in this case, which is against the trend observed for the other molecules. For β_{xyz}, all three DFT results are preferable to the HF value of −11.31, with the CCSD(T) value of −8.31 a.u. as the reference value. For $\gamma_{\parallel}$, the LB94 value of 2400 a.u. is in good agreement with the CCSD(T) number of 2312 a.u., the HF value being too low, and the LDA and BLYP values clearly too high. The comparison to the experimental γ^{EFISH} value looks good for the LB94 value as well (note the slightly different frequency compared to previous tables).

J. Comparison of β^{SHG} and γ^{EFISH} with different methods

For the β^{SHG} values gathered in Table XII, we note that, with the exception of the notorious HF molecule, there is a consistent and large overestimation for the LDA and BLYP values, ranging from 22% (CO, LDA) to 185% (NH$_3$, BLYP). These poor results are due to overestimations of both the static properties and the frequency dependence. Both are caused by the incorrect asymptotic decay of the LDA and BLYP xc potentials, as evidenced by the results obtained with the asymptotically correct LB94 potential.

TABLE XI. Results for the hyperpolarizability of CH$_4$.

	TDHF[a]	MP2[a]	CCSD[a]	CCSD(T)[a]	EXP	LDA	BLYP	LB94
β_{xyz}	−11.31	−8.14	−8.73	−8.31		−8.63	−9.45	−8.99
γ_{zzzz}	1768	2295	2138	2254		3700	4100	2300
γ_{xxzz}	638	809	763	800		1300	1400	850
$\gamma_{\parallel}$	1826[b]	2348	2198	2312		3800	4200	2400
EFISH[c]	2300[d]				3316[e]	5300	5900	3100
EOKE					2887±144	4300	4700	2600

[a]Values obtained by Maroulis (Ref. 26).
[b]Bishop and Sauer (Ref. 67) obtained 1882 at the SCF level and 2152 at the CASSCF level for the purely electronic contribution to $\gamma_{\parallel}$.
[c]Experimental value at frequency 0.06781 a.u. by Buckingham and Orr (Ref. 68). Theoretical results at the same frequency.
[d]Interpolated electronic hyperpolarizability from Bishop and Sauer (Ref. 67). At the CASSCF level they obtain 2600 a.u. (interpolated). With inclusion of vibrational effects, their values are 2718 and 3023 a.u., respectively.
[e]References 60,69–71.

TABLE XII. Average β, SHG (absolute values).

Molecule	HF	CCSD(T)+HF	EXP	LDA	BLYP	LB94
HF	5.85	8.0	10.9	10.7	11.2	7.68
CO	24.1	27.0[a]	29.9	36.6	37.8	23.4
NH$_3$	21.98	49.1	48.4	109	138	46.0
H$_2$O	12.57	21.1	21.8	34.4	37.3	20.3

[a]Maroulis (Ref. 47) obtained 30.1 a.u. in a larger basis set.

TABLE XIV. SHG percentage dispersion.

Molecule	HF	LDA	BLYP	LB94
HF	8.8	16.1	17.5	10.8
CO	14.2	20.2	21.5	13.3
NH$_3$	45.6	96.8	115.8	42.8
H$_2$O	16.4	33.7	37.6	21.3

These LB94 results show large corrections with respect to the LDA and BLYP values, substantially improving the agreement with the experimental and CCSD(T) reference values, although the LB94 values are too low in all four cases. The LB94 values are preferable to the HF results for the molecules studied here, as is clearly visible for the NH$_3$ and H$_2$O results, although the good agreement of the LB94 and experimental numbers may be somewhat fortuitous there.

For the γ^{EFISH} results in Table XIII, similar trends can be observed. The overestimations in the LDA and BLYP values are at least as large as for the β values and overestimations by a factor of two are not exceptional. This is related to the larger importance for γ of the description of the outer region of the molecule, which is poorly described by LDA and GGAs, such as BLYP. Again, the LB94 results are much better, although systematically too low, just as the HF results. The LB94 results are better than the HF results, although not for all molecules.

K. Frequency dependence for β^{SHG} and γ^{EFISH}

In Tables XIV and XV, the frequency dispersion for β^{SHG} and γ^{EFISH} is summarized. The values in the tables give the increase, in terms of percentage, of the values at $\omega = 0.0656$ a.u. (unless otherwise stated) with respect to the static ($\omega=0$) values. The four different methods discussed here show similar trends when different molecules are compared. However, the LDA and BLYP results are again too high in comparison to the LB94 results, for both β^{SHG} and γ^{EFISH}. We have previously observed this trend for the linear frequency-dependent polarizability $\alpha(\omega)$,[2] although the effect was less pronounced in that case. The LB94 percentages are close to the HF values, supporting both sets of values.

From the systematic underestimations for both of these methods, one might assume that these percentages are more probably too low than too high. However, further benchmark calculations, in which the frequency dependence is obtained from high level correlated *ab initio* methods, are needed to investigate the reliability of the LB94 and HF frequency dependencies in more detail.

IV. SUMMARY AND OUTLOOK

In this work, we have provided values for static and frequency-dependent first and second hyperpolarizabilities, using time-dependent density functional theory, for a set of 9 small molecules. We employed the adiabatic local density approximation for the xc kernels, and tested three different approximations for the xc potential: the LDA, BLYP and LB94 potentials. By employing large basis sets with many diffuse functions, we obtain values close to the basis set limit, as can be seen from comparison to numerical static LDA results in the literature. For this reason, we can draw reliable conclusions concerning the intrinsic quality of different xc potentials for determining NLO properties of small molecules. The popular LDA and BLYP xc potentials lead to systematic, large overestimations for both the static properties and the frequency dependence. This is due to the incorrect asymptotic behavior of these potentials and can be improved upon by employing an xc potential with the correct $-1/r$ behavior as r goes to infinity. The LB94 potential, which is asymptotically correct, therefore strongly improves upon the LDA and BLYP results, giving rise to values which, for the molecules studied here, improve upon the HF results in most cases. Similar to the HF results, the LB94 values tend to be underestimated for such small molecules. Our results show the importance of the choice of the xc

TABLE XIII. Average γ, EFISH at $\omega = 0.0656$ a.u.

Molecule	HF	CCSD(T)+ HF	EXP	LDA	BLYP	LB94
N$_2$	822	1100	1030	1500	1800	840
CO$_2$	910	1300	1332	2000	2500	1000
CS$_2$[a]	13680	17681	(38000)[b]	23100	20900	12200
NH$_3$	3276	5600	6147	15700	20300	4000
C$_2$H$_4$	9900	10200	9030	14500	19400	6100
CO	1211	1900	1720	2900	3200	1400
HF	359	630	830	1300	1400	470
H$_2$O	1216	2200	2310	4800	5800	1500
CH$_4$[c]	2300		2890	4300	4700	2600

[a]Values at frequency $\omega = 0.0428$ a.u. are compared here.
[b]The experimental value was obtained in a solvent, and may be a poor approximation for the gas phase value.
[c]A different frequency was used. See CH$_4$ table.

TABLE XV. EFISH percentage dispersion.

Molecule	HF	LDA	BLYP	LB94
N$_2$	12.6	20.5	22.3	14.4
CO$_2$	13.8	21.1	24.6	14.3
CS$_2$ [a]	20.3	22.8	27.6	17.4
NH$_3$	36.5	96.8	115.8	42.8
C$_2$H$_4$	52.3	58.9	75.3	34.2
CO	18.7	31.9	33.8	21.7
HF	12.2	23.3	25.9	13.4
H$_2$O	20.4	49.0	58.5	24.9
CH$_4$ [b]	26.0	38.7	41.4	29.3

[a]Different frequency used. See CS$_2$ table.
[b]Different frequency used. See CH$_4$ table.

potential, and further improvements can be expected from more refined xc potentials than LB94, which also have the correct asymptotics.

At present, one can only speculate about the exact reason for the somewhat disappointing LB94 results, which only modestly improve upon the HF values. One reason might be the poor quality of the LB94 potential nearer to the nucleus, as evidenced by the results for low-lying excitation energies,[12] which are worse than those obtained with the LDA potential, as well as the results for equilibrium geometries,[57] and dipole moments. This is certainly a point where the LB94 potential can be improved. However, it is not certain that an improvement in this respect will lead to satisfactory values. Another possibility might be that, although the LB94 potential is correct in the asymptotic region, it reaches the asymptotic $-1/r$ behavior either too fast or too slowly. An investigation concerning other asymptotically correct potentials, and possibly ''exact'' xc potentials, in the spirit of our earlier work,[6] may help to clarify this issue.

For large molecules, the LDA and BLYP overestimations due to the incorrect asymptotics can be expected to be less severe, as the importance of the outer region of the molecule decreases. For such systems, the LB94 results can be expected to be closer to the LDA and BLYP values. Although large systems need to be studied separately,[44] the improvements obtained with the LB94 results, and the expected further improvement from future xc potentials, give reason for optimism as regards the use of DFT for the determination of NLO properties.

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[1] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **103**, 9347 (1995).

[2] S. J. A. van Gisbergen, V. P. Osinga, O. V. Gritsenko, R. van Leeuwen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **105**, 3142 (1996).

[3] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, Chem. Phys. Lett. **259**, 599 (1996).

[4] V. P. Osinga, S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **106**, 5091 (1997).

[5] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, Phys. Rev. Lett. **78**, 3097 (1997).

[6] S. J. A. van Gisbergen, F. Kootstra, P. R. T. Schipper, O. V. Gritsenko, J. G. Snijders, and E. J. Baerends, Phys. Rev. A **57**, 2556 (1998).

[7] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).

[8] M. Petersilka and E. K. U. Gross, Int. J. Quantum Chem., Symp. **30**, 181 (1996).

[9] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998).

[10] M. E. Casida, in *Recent Advances in Density-Functional Methods*, edited by D. P. Chong (World Scientific, Singapore, 1995), p. 155.

[11] Ch. Jamorski, M. E. Casida, and D. R. Salahub, J. Chem. Phys. **104**, 5134 (1996).

[12] M. E. Casida, C. Jamorski, K. C. Casida, and R. D. Salahub, J. Chem. Phys. **108**, 4439 (1998).

[13] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).

[14] R. Bauernschmitt, M. Häser, O. Treutler, and R. Ahlrichs, Chem. Phys. Lett. **264**, 573 (1997).

[15] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **109**, 10644 (1998), this issue.

[16] L. Geng and J. C. Wright, Chem. Phys. Lett. **249**, 105 (1996).

[17] P. Norman, Y. Luo, D. Jonsson, and H. Ågren, J. Chem. Phys. **106**, 8788 (1997).

[18] Jianliang Li, Shufeng Wang, Hong Yang. Qihuang Gong, Xin An, Huiying Chen, and Di Qiang, Chem. Phys. Lett. **288**, 175 (1998).

[19] R. M. Dickson and A. D. Becke, J. Phys. Chem. **100**, 16105 (1996).

[20] J. Guan, P. Duffy, J. T. Carter, D. P. Chong, K. C. Casida, M. E. Casida, and M. Wrinn, J. Chem. Phys. **98**, 4753 (1993).

[21] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).

[22] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends (unpublished).

[23] E. K. U. Gross, J. F. Dobson, and M. Petersilka in *Density Functional Theory*, Springer Series in Topics in Current Chemistry, edited by R. F. Nalewajski (Springer, Heidelberg, 1996).

[24] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[25] H. Sekino and J. Bartlett, J. Chem. Phys. **98**, 3022 (1993).

[26] G. Maroulis, Chem. Phys. Lett. **226**, 420 (1994).

[27] K. Ohta, T. Sakaguchi, K. Kamada, and T. Fukumi, Chem. Phys. Lett. **274**, 306 (1997).

[28] ADF STO basis set database available online at http://tc.chem.vu.nl/SCM/DOC/atomicdata/.

[29] http://tc.chem.vu.nl/~vgisberg/basissets.html.

[30] D. M. Bishop, Adv. Quantum Chem. **25**, 3 (1994).

[31] D. P. Shelton and J. E. Rice, Chem. Rev. **94**, 3 (1994).

[32] D. A. Dixon and N. Matsuzawa, J. Phys. Chem. **98**, 3967 (1994).

[33] D. M. Bishop, Rev. Mod. Phys. **62**, 343 (1990).

[34] D. M. Bishop, B. Kirtman, H. A. Kurtz, and J. E. Rice, J. Chem. Phys. **98**, 8024 (1993).

[35] D. M. Bishop and E. K. Dalskov, J. Chem. Phys. **104**, 1004 (1996).

[36] D. M. Bishop, B. Kirtman, and B. Champagne, J. Chem. Phys. **107**, 5780 (1997).

[37] S. M. Colwell, C. W. Murray, N. C. Handy, and R. D. Amos, Chem. Phys. Lett. **210**, 261 (1993).

[38] A. M. Lee and S. M. Colwell, J. Chem. Phys. **101**, 9704 (1994).

[39] Y. Luo, O. Vahtras, H. Ågren, and P. Jørgensen, Chem. Phys. Lett. **205**, 555 (1993).

[40] C. Hättig, O. Christiansen, and P. Jørgensen, Chem. Phys. Lett. **282**, 139 (1998).

[41] G. Maroulis and A. J. Thakkar, J. Chem. Phys. **88**, 7623 (1988).

[42] B. Champagne, Chem. Phys. Lett. **287**, 185 (1998).

[43] M. P. Bogaard, A. D. Buckingham, and G. L. D. Ritchie, Mol. Phys. **18**, 575 (1970).

[44] B. Champagne, E. A. Perpète, S. J. A. van Gisbergen, E. J. Baerends, J. G. Snijders, C. Soubra-Ghaoui, K. Robins, and B. Kirtman, J. Chem. Phys. **109**, 10489 (1998).

[45] J. F. Ward and C. K. Miller, Phys. Rev. A **19**, 826 (1979).

[46] F. Aiga and R. Itoh, Chem. Phys. Lett. **251**, 372 (1996).

[47] G. Maroulis, J. Phys. Chem. **100**, 13466 (1996).

[48] P. Lazzeretti and R. Zanasi, J. Chem. Phys. **74**, 5216 (1981).

[49] J. W. Dudley and J. F. Ward, J. Chem. Phys. **82**, 4673 (1985).

[50] C. Hättig, O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **269**, 428 (1997).

[51] P. B. Rozyczko and R. J. Bartlett, J. Chem. Phys. **107**, 10823 (1997).

[52] M. G. Papadopoulos, J. Waite, and A. D. Buckingham, J. Chem. Phys. **102**, 371 (1995).

[53] G. Maroulis, Chem. Phys. Lett. **289**, 403 (1998).

[54] P. Kaatz, E. A. Donley, and D. P. Shelton, J. Chem. Phys. **108**, 849 (1998).

[55] G. Maroulis, J. Chem. Phys. **94**, 1182 (1991).

[56] Y. Luo, H. Ågren, O. Vahtras, P. Jørgensen, V. Spirko, and H. Hettema, J. Chem. Phys. **98**, 7159 (1993).

[57] R. Neumann, R. H. Nobes, and N. C. Handy, Mol. Phys. **87**, 1 (1996).

[58] J. F. Ward and G. H. C. New, Phys. Rev. **185**, 57 (1969).

[59] Y. Mizrahi and D. P. Shelton, Phys. Rev. Lett. **55**, 696 (1985).

[60] Y. Mizrahi and D. P. Shelton, Phys. Rev. A **31**, 3145 (1985).

[61] A. D. Buckingham, M. P. Bogaard, D. A. Dunmur, C. Hobbs, and B. J. Orr, Trans. Faraday Soc. **66**, 1548 (1970).

[62] J. F. Ward and D. S. Elliott, J. Chem. Phys. **69**, 5438 (1978).

[63] B. F. Levine and C. G. Bethea, J. Chem. Phys. **63**, 2666 (1975).

[64] H. Sekino and J. Bartlett, Chem. Phys. Lett. **234**, 87 (1995).

[65] R. Kobayashi, H. Koch, P. Jørgensen, and T. J. Lee, Chem. Phys. Lett. **211**, 94 (1993).

[66] D. M. Bishop and G. Maroulis, J. Chem. Phys. **82**, 2380 (1985).

[67] D. M. Bishop and S. P. A. Sauer, J. Chem. Phys. **107**, 8502 (1997).

[68] A. D. Buckingham and B. J. Orr, Trans. Faraday Soc. **65**, 673 (1969).

[69] D. P. Shelton, Phys. Rev. A **34**, 304 (1986).

[70] D. P. Shelton, Phys. Rev. A **42**, 2578 (1990).

[71] D. P. Shelton and J. J. Palubinskas, J. Chem. Phys. **104**, 2482 (1996).